

Improved Slater approximation to SIC-OEP

J. Messud^a, P. M. Dinh^{a*}, P.-G. Reinhard^b, and E. Suraud^a

^a*Laboratoire de Physique Théorique, Université Paul Sabatier, CNRS, F-31062
Toulouse Cédex, France*

^b*Institut für Theoretische Physik, Universität Erlangen, D-91058 Erlangen,
Germany*

Abstract

We propose a simplification of the Optimized Effective Potential (OEP) method applied to the Self Interaction Correction (SIC) on the Local Density Approximation (LDA) in Density Functional Theory (DFT). The new scheme fulfills crucial formal key properties. It turns out to be simple and accurate. We apply the new method to a schematic model for a dimer molecule and to the C atom. We discuss observables which are especially sensitive to details of the SIC.

Key words: Density Functional Theory, Self-Interaction Correction, Optimized Effective Potential, Slater approximation

PACS: 71.15.Mb, 31.15.E-, 73.22.-f, 31.15.ap

1 Introduction

Density-functional theory (DFT) is a major tool for the description of electronic systems as, e.g., atoms, molecules, solids, or chemical reactions [1]. It simplifies the involved many-electron problem and thus allows to compute rather complex systems, for a general overview see [2,3]. Most applications employ energy-density functionals based on the Local Density Approximation (LDA), see e.g. [4], or its extension to the generalized gradient approximation (GGA) [5]. In spite of their success, these approaches have still deficiencies. In particular, the self-interaction error spoils single-particle properties as, e.g., the Ionization Potential (IP) or the band gap in solids [6,7]. Another critical detail where LDA and GGA fail is the polarizability in chain molecules [8,9].

* Corresponding author

Email-address : dinh@irsamc.ups-tlse.fr

A way out of the self-interaction problem is to use exact exchange. That, however, is an order of magnitude more expensive and it causes problems with a reliable description of the remaining correlation effects [10]. An intuitive and efficient solution, still close to the spirit of DFT, is to augment LDA by a Self-Interaction Correction (SIC) [11,12]. That, on the other hand, produces a state-dependent mean-field Hamiltonian which requires extra measures to maintain orthogonality of the single particle basis [12,13,14,15]. The desirable goal remains to have a common local mean-field potential $V(\mathbf{r})$. That goal is reached through the optimized effective potential (OEP) method, see [16,17] for early proposals, and [10] for an extensive recent review. There exist OEP approaches based on exact exchange but these are still rather involved, as exchange is. In that case, OEP serves mainly to produce a well defined single-particle spectrum in occupied space as well as in unoccupied space [18,19]. But OEP is also a useful means to overcome the difficulties of SIC, see e.g. [20,21,22]. Indeed it is found that OEP manages to maintain crucial features of the underlying SIC (or exact exchange) as, e.g., the localization of states or the derivative discontinuity [23,24,25]. The involved SIC-OEP equations are thus often simplified. Popular is, e.g., the Krieger-Li-Iafrate (KLI) approach [20,21] and, in a further step of simplification, the Slater approximation [16]. However, KLI and Slater approximation can easily miss crucial features of SIC as, e.g., the localization of states and the performance with respect to polarizability [8,9].

It is the aim of this paper to propose a scheme for SIC-OEP which allows to deal with the Slater approximation to OEP while maintaining key features of the full SIC scheme. The new move is to allow for a double set of occupied single-particle states. The two sets are connected by a unitary transformation such that both sets build the same total density. The first of the sets consists of the solutions of the SIC-OEP equations and is thus diagonal in energy. The second set is used to compute the total SIC energy. The distinction between the two sets allows the second set to develop spatially localized states which is energetically advantageous for the SIC energy functional. The localization of the second set validates the Slater approximation to OEP. We call the new scheme “generalized Slater approximation”. We present it after briefly reviewing SIC-OEP, SIC as such, and a variant of SIC which already employs the double set of single-particle states. The method is applied to a schematic model for a dimer molecule and to the C atom. We will compare exact Hartree-Fock with all relevant approximations (LDA, SIC, Slater and generalized Slater). In all the following, we employ, in fact, the local spin-density approximation but denote it with the simpler term LDA (rather than the sometimes used more complete abbreviation LSDA).

2 SIC without approximations

The starting point for all following considerations is the SIC energy functional for electrons, which reads

$$E_{\text{SIC}} = E_{\text{kin}} + E_{\text{ion}} + E_{\text{LDA}}[\rho] - \sum_{\beta=1}^N E_{\text{LDA}}[\rho_{\beta}] \quad (1)$$

where $E_{\text{LDA}}[\rho]$ is a standard energy-density functional in LDA complementing the kinetic energy E_{kin} and the interaction energy with the ionic background E_{ion} . The last term therein is the SIC term. The densities are defined from the single-particle states ψ_{β} , i.e. $\rho = \sum_{\beta} \rho_{\beta}$ with $\rho_{\beta} = |\psi_{\beta}|^2$. All summations run over occupied states only.

Two features of the SIC energy (1) are to be noted. First, it is not invariant under unitary transformations amongst the occupied states because the SIC term is sensitive to each single-particle state separately. Second, the SIC induces a tendency to localized single-particle states. Given a total density ρ , the distribution over several ρ_{β} produces maximal Coulomb energy if these ρ_{β} are localized. Such a localization is found in many studies of SIC [26] or SIC-OEP [10]. This feature will play a crucial role in the following considerations.

The mean-field equations are derived from the total energy (1) by variation with respect to the single-particle states ψ_{α}^* . In the general case, the mean-field Hamiltonian becomes

$$\hat{h}_{\alpha} = \hat{h}^{(\text{LDA})} - U_{\alpha}(\mathbf{r}) \quad , \quad (2a)$$

$$U_{\alpha}(\mathbf{r}) = \frac{\delta E_{\text{LDA}}[\rho_{\alpha}]}{\delta \rho_{\alpha}(\mathbf{r})} = U_{\text{LDA}}[|\psi_{\alpha}|^2] \quad , \quad (2b)$$

$$\hat{h}^{(\text{LDA})} = \frac{\hat{p}^2}{2m} + \frac{\delta E_{\text{LDA}}[\rho]}{\delta \rho(\mathbf{r})} \quad , \quad (2c)$$

where the first term is the standard LDA mean field and the second term, state-dependent, stems from the SIC term in the energy (1).

2.1 SIC with single set

The SIC mean-field Hamiltonian (2) is state-dependent. A direct solution of the Schrödinger equation with a state-dependent Hamiltonian can lead to non-orthogonal single-particle states. This, however, violates basic requirements of DFT. One has to enforce orthonormality by a constraint, thus minimizing

$E_{\text{SIC}} - \sum_{\alpha\beta} \lambda_{\alpha\beta} (\psi_\alpha | \psi_\beta)$ where $\lambda_{\alpha\beta}$ is a matrix of Lagrangian multipliers, which is non-diagonal in general. By straightforward variational techniques, we then obtain the stationary SIC equations :

$$\hat{h}_{\text{SIC}} |\psi_\alpha\rangle = \sum_{\beta} |\psi_\beta\rangle \lambda_{\beta\alpha} , \quad (3a)$$

$$\lambda_{\beta\alpha} = (\psi_\beta | \hat{h}_{\text{SIC}} | \psi_\alpha) , \quad (3b)$$

$$0 = (\psi_\beta | U_\beta - U_\alpha | \psi_\alpha) , \quad (3c)$$

$$\hat{h}_{\text{SIC}} = \hat{h}_{\text{LDA}} - \sum_{\alpha} U_\alpha |\psi_\alpha\rangle \langle \psi_\alpha| , \quad (3d)$$

where we have packed the state-dependence into projector notation in the SIC mean field (3d). This yields a formally compact notation of \hat{h}_{SIC} . Note that Eq. (3a) is not an eigenvalue equation because the matrix of Lagrange multipliers may possibly become non-diagonal. This equation as such thus does not provide a valuable starting basis for developing an OEP scheme, which requires implicitly an eigenvalue equation [17]. A key part in the SIC equations (3) is the symmetry condition (3c). It emerges as follows : The Lagrangian matrix is real symmetric, $\lambda_{\alpha\beta} = \lambda_{\beta\alpha}$, because the overlap matrix $(\psi_\alpha | \psi_\beta)$ has that feature. Thus the hermitian conjugate of (3a) becomes $(\psi_\beta | \hat{h}_{\text{SIC}}^\dagger = \sum_{\alpha} \lambda_{\beta\alpha} \langle \psi_\alpha |$. We take the difference. The $\lambda_{\beta\alpha}$ cancel out and we remain with $0 = (\psi_\beta | \hat{h}_{\text{SIC}}^\dagger - \hat{h}_{\text{SIC}} | \psi_\alpha)$ which then yields the symmetry condition (3c). It is a highly non-linear equation requiring an involved solution strategy. But formally, the symmetry condition simply emerges from minimizing the total energy in a reduced space of orthonormalized single-particle orbitals. This minimization principle also implies that there always exists a solution to the symmetry condition, in spite of its apparent complexity.

2.2 SIC with double basis set

The SIC equations (3) do not yield immediately single-particle energies and associated “energy-diagonal” states. It is plausible that the matrix $\lambda_{\beta\alpha}$ contains the relevant information. The idea is thus that diagonalization of $\lambda_{\beta\alpha}$ yields the desired single-particle energies together with energy-diagonal states φ_i . These energy-diagonal states tend naturally to larger spatial width and will not remain as localized as the SIC basis states ψ_α . Both sets have their virtues but they cannot be identical due to the state-dependence of the SIC mean field. This suggests to introduce throughout a second basis set φ_i which is related to the set ψ_α by a unitary transformation within occupied space, i.e.

$$\psi_\alpha = \sum_{i=1}^N \varphi_i u_{i\alpha} . \quad (4a)$$

We exploit the freedom of a unitary transformation $u_{i\alpha}$ to choose a basis which diagonalizes the constraint matrix $\lambda_{\beta\alpha}$. This then yields the diagonal SIC equations

$$\hat{h}_{\text{SIC}}|\varphi_i) = \varepsilon_i|\varphi_i) \quad . \quad (4b)$$

together with the symmetry condition

$$u_{i\alpha} : \quad 0 = (\psi_\beta|U_\beta - U_\alpha|\psi_\alpha) \quad , \quad (4c)$$

which now serves to determine the coefficients $u_{i\alpha}$ of the transformation (4a) for given φ_i . Note that the symmetry condition (4c) looks similar to Eq. (3c), but is used somewhat differently here, namely to define the coefficients of the unitary transformation (4a). The \hat{h}_{SIC} is defined in detail by the SIC equations (3). The new Eqs. (4) combine the solution of the former SIC equations, yielding the ψ_α , with the direct evaluation of the energy-diagonal basis. What expense is concerned, there is no advantage as compared to the previous scheme, i.e. solving first the SIC equations and diagonalizing then the constraint matrix $\lambda_{\beta\alpha}$ in a second step. But it serves from a formal point of view as a preparatory step for SIC-OEP. Although Eq. (4b) is an eigenvalue equation, the corresponding Hamiltonian \hat{h}_{SIC} is obviously non-local, see Eq. (3d), which complicates the numerical handling. This is why approximations have been searched for since long in order simplify calculations.

3 SIC-OEP

3.1 SIC-OEP with double set

In section 2.2, we have shown that the definition of single-particle energies in connection with SIC naturally leads to the introduction of a double set of single-particle states connected by a unitary transformation. We transfer now this generalization to OEP. The idea beyond SIC-OEP is the following. We start from a set $\tilde{\varphi}_i$, being solution of the OEP equations :

$$\left[\hat{h}^{(\text{LDA})}(\mathbf{r}) - V_0(\mathbf{r}) \right] \tilde{\varphi}_i(\mathbf{r}) = \varepsilon_i \tilde{\varphi}_i(\mathbf{r}) \quad , \quad (5)$$

where V_0 is a local and state-independent potential which needs to be optimized to minimize the SIC energy, Eq. (1). Formally, this amounts to parameterize the SIC wavefunctions through V_0 , to consider the SIC energy as a functional of V_0 , and to perform variation with respect to V_0 . The $|\tilde{\varphi}_i)$ can thus be written as $|\varphi_i^{V_0})$ and these are associated to the corresponding set of $|\psi_\alpha^{V_0})$ connected by the unitary transformation Eq. (4a). For the sake of simplicity, we keep in the following the notation $|\tilde{\varphi}_i)$ for the $|\varphi_i^{V_0})$ and use correspondingly $|\psi_\alpha)$ for $|\psi_\alpha^{V_0})$.

The optimized effective potential $V_0(\mathbf{r})$ is then found by variation $\delta E_{\text{SIC}}/\delta V_0(\mathbf{r}) = 0$. One can show that the thus optimized V_0 can be written as a sum of three contributions :

$$V_0 = V_S + V_K + V_C \quad , \quad (6a)$$

$$V_S = \sum_i \frac{|\tilde{\varphi}_i|^2}{\rho} v_i \quad , \quad (6b)$$

$$V_K = \sum_i \frac{|\tilde{\varphi}_i|^2}{\rho} (\tilde{\varphi}_i | V_0 - v_i | \tilde{\varphi}_i) \quad , \quad (6c)$$

$$V_C = \frac{1}{2} \sum_i \frac{\nabla \cdot (p_i \nabla |\tilde{\varphi}_i|^2)}{\rho} \quad , \quad (6d)$$

with the density $\rho = \sum_i |\tilde{\varphi}_i|^2$. The term V_S is the Slater contribution, $V_K + V_S$ constitutes the KLI approximation, and V_C is the remaining genuine OEP term. The quantities v_i and p_i entering the various contributions are defined as

$$v_i = \sum_{\alpha} u_{i\alpha}^* \frac{\tilde{\psi}_{\alpha}}{\tilde{\varphi}_i} U_{\alpha} \quad , \quad (7a)$$

$$p_i(\mathbf{r}) = \int d\mathbf{r}' \{V_0(\mathbf{r}') - v_i(\mathbf{r}')\} \frac{\tilde{\varphi}_i(\mathbf{r}')}{\tilde{\varphi}_i(\mathbf{r})} G_i(\mathbf{r}, \mathbf{r}') \quad , \quad (7b)$$

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\tilde{\varphi}_j^*(\mathbf{r}) \tilde{\varphi}_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} \quad . \quad (7c)$$

Inserting (4a) and (7a) in the quantities involved in (6b-6d), one obtains :

$$V_S = \sum_{\alpha} \frac{|\tilde{\psi}_{\alpha}|^2}{\rho} U_{\alpha} \quad , \quad (8a)$$

$$(\tilde{\varphi}_i | V_0 - v_i | \tilde{\varphi}_i) = \sum_{\alpha, \beta} u_{i\alpha}^* u_{i\beta} (\tilde{\psi}_{\beta} | V_0 - U_{\alpha} | \tilde{\psi}_{\alpha}) \quad , \quad (8b)$$

$$p_i(\mathbf{r}) = \sum_{\alpha} u_{i\alpha}^* \int d\mathbf{r}' (V_0(\mathbf{r}') - U_{\alpha}(\mathbf{r}')) \frac{\tilde{\psi}_{\alpha}(\mathbf{r}')}{\tilde{\varphi}_i(\mathbf{r})} G_i(\mathbf{r}, \mathbf{r}') \quad , \quad (8c)$$

We now exploit the interesting property that the $\tilde{\psi}_{\alpha}$ are localized [26]. This means that, at a given \mathbf{r} , one single $\tilde{\psi}_{\alpha}$ mostly dominates the other wave-functions $\tilde{\psi}_{\beta}$. This amounts to have almost vanishing (8b) and (8c), and thus allows to neglect in V_0 the two terms V_K and V_C defined in Eqs. (6c) and (6d) respectively. The final OEP result thus naturally reduces to

$$\varepsilon_i \tilde{\varphi}_i(\mathbf{r}) = [\hat{h}^{(\text{LDA})}(\mathbf{r}) - V_0(\mathbf{r})] \tilde{\varphi}_i(\mathbf{r}) \quad , \quad (9a)$$

$$V_0 \simeq \sum_{\alpha} \frac{|\tilde{\psi}_{\alpha}|^2}{\rho} U_{\text{LDA}}[|\tilde{\psi}_{\alpha}|^2] \quad , \quad (9b)$$

$$0 = (\tilde{\psi}_{\beta} | U_{\text{LDA}}[|\tilde{\psi}_{\alpha}|^2] - U_{\text{LDA}}[|\tilde{\psi}_{\beta}|^2] | \tilde{\psi}_{\alpha}) \quad , \quad (9c)$$

$$\tilde{\psi}_{\alpha} = \sum_i \tilde{\varphi}_i u_{i\alpha} \quad , \quad (9d)$$

with the symmetry condition (9c) explicitly rewritten for completeness. The mean field equation (9a) generates the set $\tilde{\varphi}_i$ of occupied states, while the unitary transformation (9d) serves to accommodate the symmetry condition (9c) which, in turn, defines the “localized” set $\tilde{\psi}_{\alpha}$ that enters the Slater mean field V_0 as given in Eq. (9b). Note that this equation has the form of a Slater approximation [24,27] but is constructed from the localized $\tilde{\psi}_{\alpha}$ and applied to the $\tilde{\varphi}_i$. We thus call this new scheme “Generalized SIC Slater” approximation, which differs from the usual Slater scheme because of the two basis sets involved here.

3.2 Recovering “standard” SIC-OEP

The SIC-OEP scheme presented in section 3.1 differs from usual SIC-OEP formulations in that it employs simultaneously two complementing sets of orbitals $\tilde{\psi}_{\alpha}$ and $\tilde{\varphi}_i$. It is instructive to step back to “standard” SIC-OEP. Indeed the recovery procedure sheds some light on the relevance of approximations performed in standard SIC-OEP approaches. One recovers the standard formulation by simply setting the unitary transform Eq. (4a) to unity, i.e.,

$$u_{i\alpha} \rightarrow \delta_{i\alpha} \quad (10)$$

which renders the sets $\tilde{\psi}_{\alpha}$ and $\tilde{\varphi}_i$ identical. The symmetry condition becomes obsolete because there is no unitary transformation to be optimized. The crucial v_i then simply reduces to $U_{\text{LDA}}[|\tilde{\varphi}_i|^2]$, see Eq. (2b), and the usual Slater and KLI approximations are directly obtained from Eqs. (6a-6c). KLI means to approximate $V_0 \approx V_S + V_K$ while the usual Slater approximation goes one step further to $V_0 \approx V_S$, but then applied in a situation with only one set of wavefunctions.

The usual reasoning to validate the KLI approximation, i.e., neglecting the correction term (6d), relies on the oscillating nature of $\mathbf{p}_i(\mathbf{r})$ which makes it small in the average. Going from KLI to Slater is then usually justified only in the case of homogeneous or well localized systems (described by $\tilde{\varphi}_i$). Our Generalized Slater potential, as built from localized orbitals (described by $\tilde{\psi}_{\alpha}$), thus naturally appears as a good and well justified approximation to full OEP. It remains to see how it performs in actual computations.

4 Test for a 1D dimer molecule

As first applications of the generalized Slater approximation, we consider two test cases. First, we consider a dimer molecule in one dimension (1D) which is a widely used schematic model for critically probing crucial structural and dynamical features of an approach, see e.g. [28]. In particular the studies of [29] have shown that 1D models carry all features of (de-)localization. The two electrons in the dimer have the same spin in order to test the exchange term and the self-energy error. As an interaction, we use a smoothed Coulomb potential, $w_{ij} = e^2 / \sqrt{(x_i - x_j)^2 + a_{ij}^2}$, where the parameters a_{ij} for electron-electron, electron-ion and ion-ion interactions are tuned to reproduce typical molecular energies. Taking this interaction, we develop within LDA an energy functional for the exchange term. Working at the level of exchange only allows to have Hartree-Fock (HF) calculations as a benchmark to which approximations can be compared. The second test case will be naturally a "localized" system with more electrons, namely a C atom with 4 electrons (3 spins up and 1 down), computed in realistic three dimensions.

Fig. 1 shows the result for the dimer case. One finds in the upper panel the dimer binding energy $E_{\text{bond}} = E_{\text{dimer}} - 2E_{\text{atom}}$ as a function of atomic distance for the various approximations. The lower panel shows the dipole polarizability α_D which is a sensitive test for DFT considerations [30,31]. The dimer binding energy in Slater approximation (dashed-dotted curve) shows an unnatural bump with a maximum at distance of $5 a_0$. This is caused by a trend to delocalization in this approximation. The same feature happens in KLI (not shown here). SIC instead, which has a tendency to localization, produces a reasonable energy curve (dotted line under the full curve) close to the exact HF case (full line). It is gratifying to see that the generalized Slater approximation (full curve labeled "GSlat", almost identical to the SIC one) performs equally well. The simple-most LDA does also perform fairly well what the dimer binding curve is concerned (dashed line almost identical to the SIC one). A different perspective is provided by the results for the polarizability. LDA is notoriously off the benchmark HF result. SIC performs very well. SIC-Slater, however, fails again. But generalized Slater (full curve) does follow the SIC result nicely for physically relevant bond distances.

Fig. 2 analyzes the findings by comparing the terms neglected when stepping from OEP down to (generalized) Slater. Mainly because of the oscillating behavior of p_i defined in Eq. (7b), the mean values of V_K and V_C are very small. Thus we plot in Fig. 2 their root-mean-square expectation value, i.e. $\sqrt{\langle V_i^2 \rangle}$ with $\langle V_i^2 \rangle = \int dx V_i^2(x)$, normalized by that of V_S . The r.m.s. expectation value of the KLI term V_K is generally smaller than that of V_C . The gain in smallness by generalized Slater is dramatic (mind the percentage scale). Even there, one observes some growth of the r.m.s. expectation value of V_C for small

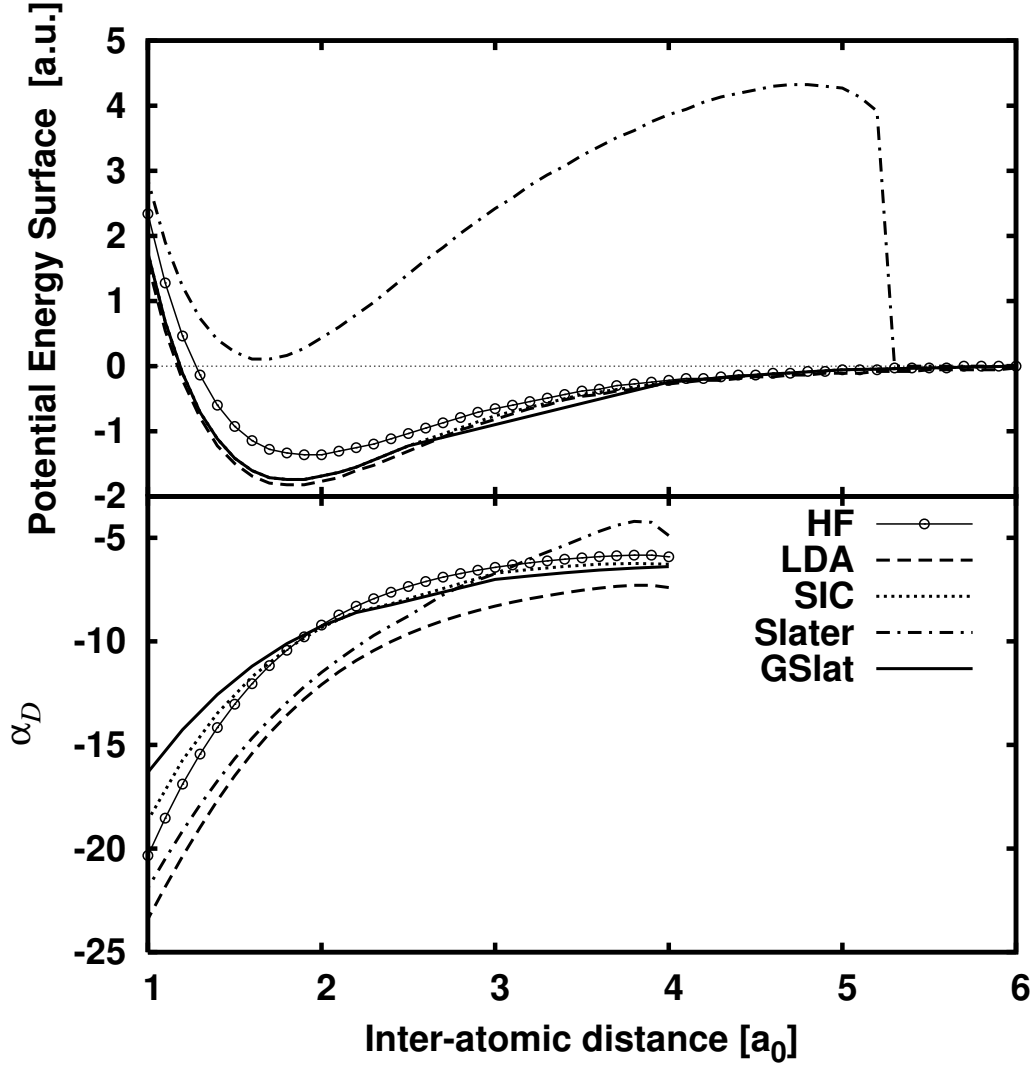


Fig. 1. Upper : Born-Oppenheimer surface for a 1D dimer molecule with two electrons. Compared are results from HF, LDA, SIC, usual Slater approximation, and the generalized Slater approximation (GSlat). Lower : Polarization as a function of inter-atomic distance for the five approximations considered.

distances. This coincides with the deviation in the polarizability observed in Fig. 1 for very small distances.

As a test case for a compact electron distribution, we have considered the C atom using fully three dimensional calculations [32]. The starting point is a calculation with exact exchange and the approximations are compared consistently with LDA for exchange only. Fig. 3 shows the relative deviations for energy and polarizabilities α (note that the electron cloud is slightly asymmetric such that α depends on the spatial direction). The conclusion is obvious. SIC is a good approximation to the exact calculation and generalized Slater does equally well, while simple Slater or LDA show larger deviations.

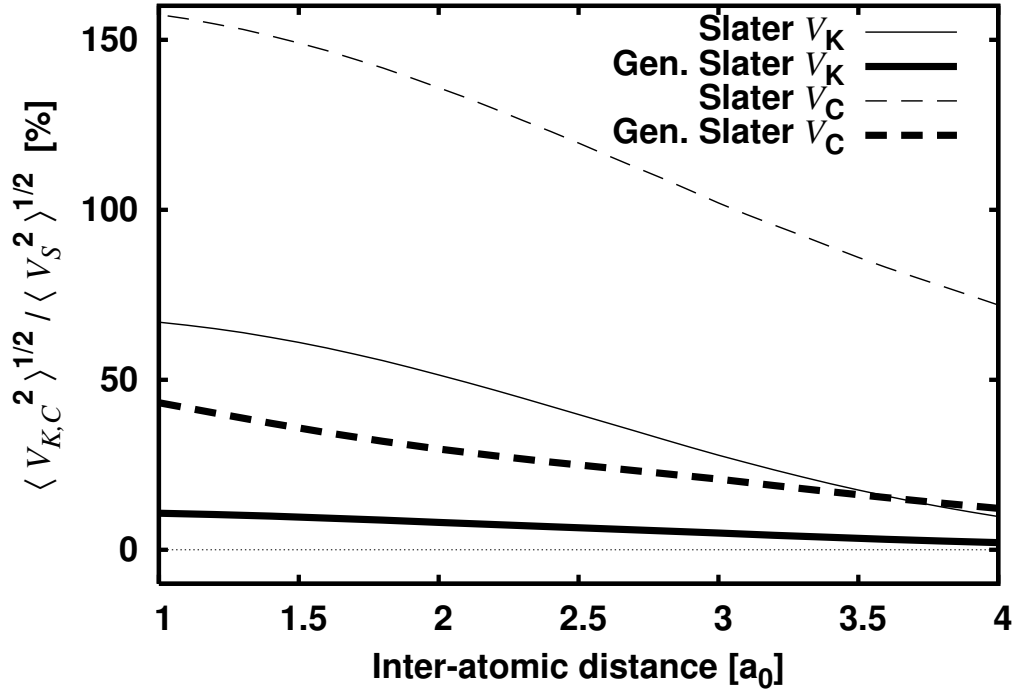


Fig. 2. R.m.s. expectation value of the neglected KLI-OEP terms, V_K and V_C , rescaled by that of the Slater potential V_S : in the usual Slater approximation (thin curves), see Eqs. (6c,6d), and in our generalized Slater one (thick curves), calculated as in Eqs. (6c,6d) but with the $\tilde{\psi}_\alpha$ instead of the $\tilde{\varphi}_i$. Results for the 1D dimer molecule with two electrons are drawn versus inter-atomic distance and are given in percentages.

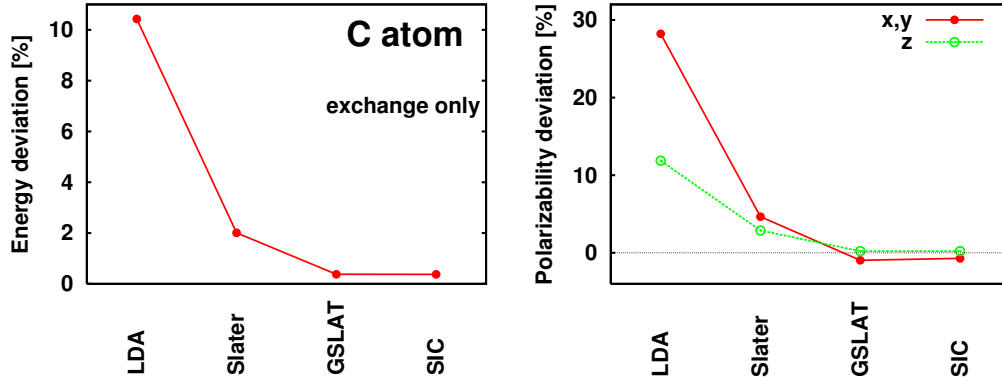


Fig. 3. Comparison of various approaches for the C atom. Left panel: Deviation of binding energy from the Hartree-Fock benchmark value. Right panel: Deviation of dipole polarizabilities (in x , y , and z direction) from the Hartree-Fock values.

5 Conclusion and outlook

We have presented a formulation of SIC-OEP which employs two different sets of N single-particle wavefunctions. One set is taken for the solution of the OEP

equations, thus diagonal in energy and most likely delocalized. The other set is used in setting up the SIC energy which becomes minimal for localized wavefunctions. Both sets are connected by a unitary transformation which leaves key features as, e.g, the total density invariant. Using that double set allows to accommodate two conflicting demands, energy diagonality versus locality. The unitary transformation is determined by minimization of the SIC energy which leads to what we called the symmetry condition, a key building block of the SIC equations. The localized character of the SIC-optimizing set is well suited to justify the steps from OEP to KLI and further to Slater approximation. We call that scheme generalized Slater approximation. By virtue of the double-set technique, it has a wider range of applicability than straightforward KLI or Slater approximation. We have tested the scheme on a 1D model of a dimer at various distances and on the C atom in full 3D, comparing LDA, standard Slater approximation, generalized Slater approximation, and SIC with full Hartree-Fock as a benchmark. The numerical tests demonstrate that the generalized Slater approximation performs remarkably well. The present development is to be considered as a first step. A generalization to a time-dependent version is obvious, but raising several new consistency conditions (energy conservation, stability). Work in that direction is in progress.

This work was supported, by Agence Nationale de la Recherche (ANR-06-BLAN-0319-02), the Deutsche Forschungsgemeinschaft (RE 322/10-1), and the Humboldt foundation.

References

- [1] W. Kohn, Rev. Mod. Phys. **71** (1999) 1253.
- [2] R G Parr, W Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
- [3] R. M. Dreizler, E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem*, Springer-Verlag, Berlin, 1990.
- [4] R. O. Jones, O. Gunnarsson, Rev. Mod. Phys. **61** (1989) 689.
- [5] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77** (1996) 3865.
- [6] M. S. Hybertsen, S. G. Louie, Phys. Rev. B **34** (1986) 5390.
- [7] R. M. Nieminen, Current Opinion in Solid State and Materials Science, **4** (1999) 493.
- [8] S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, J. G. Snijders, B. Champagne, B. Kirtman, Phys. Rev. Lett. **83** (1999) 694.
- [9] S. Kümmel, L. Kronik, J. P. Perdew, Phys. Rev. Lett. **93** (2004) 213002.

- [10] S. Kümmel, L. Kronik, Rev. Mod. Phys. **80** (2008) 3.
- [11] J.P. Perdew, Chem. Phys. Lett. **64** (1979) 127.
- [12] J.P. Perdew, A. Zunger, Phys. Rev. B **23** (1981) 5048.
- [13] J. G. Harrison, R. A. Heaton, C. C. Lin, J. Phys. B **16** (1983) 2079.
- [14] A. Svane, O. Gunnarsson, Phys. Rev. Lett. **65** (1990) 1148.
- [15] S. Goedecker, C.J. Umrigar, Phys. Rev. A **55** (1997) 1765.
- [16] R. T. Sharp, G. K. Horton, Phys. Rev. **90** (1953) 317.
- [17] J. D. Talman, W. F. Shadwick, Phys. Rev. A **14** (1976) 36.
- [18] A. Görling, Phys. Rev. Lett. **83** (1999) 5459.
- [19] F. Della Sala, A. Görling, J. Chem. Phys. **115** (2001) 5718.
- [20] J.B. Krieger, Y. Li, G. J. Iafrate, Phys. Rev. A **45** (1992) 101.
- [21] J.B. Krieger, Y. Li, G. J. Iafrate, Phys. Rev. A **46** (1992) 5453.
- [22] C. A. Ullrich, U. J. Gossmann, E. K. U. Gross, Phys. Rev. Lett. **74** (1995) 872.
- [23] J. P. Perdew, M. Levy, Phys. Rev. Lett. **51** (1983) 1884.
- [24] J. B. Krieger, Y. Li, G. J. Iafrate, Phys. Lett. A **146** (1990) 256.
- [25] M. Mundt, S. Kümmel, Phys. Rev. Lett. **95** (2005) 203004.
- [26] M. Pederson, R. A. Heaton, C. C. Lin, J. Chem. Phys. **80** (1984) 1972.
- [27] J. C. Slater, Phys. Rev. **81** (1951) 385.
- [28] H. Yu, T. Zuo, A. D. Bandrauk, Phys. Rev. A **54** (1996) 3290.
- [29] M. Mundt, S. Kuemmel, Phys. Rev. A **74** (2006) 022511.
- [30] O. V. Gritsenko, E. J. Baerends, Phys. Rev. A **64** (2001) 042506.
- [31] M. Grüning, O. V. Gritsenko, E. J. Baerends, J. Chem. Phys. **116** (2002) 6435.
- [32] F. Calvayrac, P.-G. Reinhard, E. Suraud, and C. A. Ullrich, Phys. Rep. **337** (2000) 493.